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THE AFTER-COOKING DISCOLORATION

OF POTATOES-
A Review

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By E. Yanovsky

Table of Contents

1.	The Problem	Page
١.	THE PROBLEM	1
2.	Introduction	1
3.	Relation of Variety, Soil, and Fertilizers to Blackening of Potatoes	2
4.	Relation of Climate and Irrigation to Blackening of Potatoes	7
5.	Potato Storage and Blackening	8
6.	Potato Composition and Blackening	9
7.	Measurement of Discoloration	11
8.	Predetermination of Blackening of Potatoes on Boiling	12
9.	Suggestions for Preventing Discoloration in Cooked or Processed Potatoes	13
0.	Mechanism of Discoloration and the Nature of Coloring Matter	14
1.	Summary	20
2.	References	21

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THE PROBLEM

Quite often a healthy looking potato tuber will discolor after it is boiled. The discoloration will appear soon after cooling. It usually starts at the stem end of the tuber as a gray, blue, or black spot which, in some cases, gradually spreads over the surface. For this reason the discoloration is called stem-end blackening, or just blackening or graying. The potatoes showing such discoloration are sometimes called abnormal potatoes, as contrasted with normal potatoes which do not discolor after boiling. This phenomenon is met with more often in the eastern and midwestern parts of this country, rarely in the farwestern potato producing areas. The problem also exists in Canada, Great Britain, Germany, The Netherlands, and undoubtedly in other potato producing countries. It is an endemic phenomenon in many localities, occasionally assuming epidemic proportions.

Various studies (18, 42)2/of the consumers preferences for potatoes showed that mealiness and absence of blackening are considered as most desirable cooking qualities by both household and institution buyers. Since blackening appears also in canned, dehydrated, frozen, and other industrial potato products, the importance of this problem becomes obvious.

INTRODUCTION

In 1953 Lawson (20) published a brief review of the literature (with 22 references) on the subject of blackening of potatoes on cooking. The present review is somewhat more detailed and the list of references more complete. It should, however, be considered primarily as a review of British and American literature on the subject. One Dutch and two German articles do not cover the entire literature on the discoloration of potatoes in these countries and, undoubtedly, other potato producing countries have their literature on this subject. In a forthcoming publication, on discoloration of potatoes by Kiermeier and Rickerl (in Zeit Lebensmittel), a number of foreign articles not mentioned in this review are cited.

¹ A LABORATORY OF THE EASTERN UTILIZATION RESEARCH BRANCH, AGRICULTURAL RESEARCH SERVICE, U. S. DE-PARTMENT OF AGRICULTURE.

² Number in parentheses refers to References, page 21,

Various factors or combination of factors which might affect the blackening of potatoes are considered under different headings, but the nature of the subject is such that some overlapping could not be avoided.

In 1940 Nash and Smith wrote (27): "A review of literature dealing with factors affecting cooking quality (of potatoes) leaves one extremely confused. There is scarcely a single factor which is supposed to affect cooking quality that is not upheld by some investigators and discarded by others. Very little is known with much degree of certainty as to the effect of different environmental and nutritional factors on cooking quality." Perusal of the following pages will show that the above statement is still valid.

RELATION OF VARIETY, SOIL, AND FERTILIZERS TO BLACKENING OF POTATOES

In 1905 and 1904 Ashby (1) grew potatoes in Great Britain on two lots in the same locality but on different soils, using identical fertilizer applications on both lots. Mechanical analysis of the soils showed that potatoes with more blackening were obtained from soils deficient in finest particles, but the correlation was rather weak. There was no correlation between the chemical composition of soil (analyzed for nitrogen, potassium, phosphorus, calcium, magnesium, iron, and manganese) and cooking quality of the potatoes, except perhaps, for some indication that soils low in potash yield poor quality potatoes. The author's conclusion was: "Nothing conclusive as regards that aspect of quality (blackening) has been arrived at."

Wallace (55) tested potash fertilizer on early and late potatoes in Great Britain. He found that either potassium chloride or potassium sulfate added to the fertilizer was beneficial as far as the elimination of blackening was concerned. The control on late potatoes with only nitrogen and phosphorus in the fertilizer showed considerable blackening.

Findlay (14), in observing the growth of a number of varieties of potatoes in Scotland, noticed that more potatoes blackened on cooking when potash was omitted from the fertilizer. Findlay remarked that the growers pay more attention to the yield than to the quality of potatoes.

Merkenschlager (23) described results obtained by growing potatoes of the same variety on two plots in Holland. Potash was omitted from the fertilizer for one of the plots. Out of ten tubers from the potash plot, only one showed a slight discoloration after cooking. Only one of ten tubers from the potash-deficient plot remained white; the others showed various degrees of blue or black discoloration.

Merkenschlager (22) states that some varieties have a greater tendency to blacken than others.

Tottingham, Nagy, and Ross (44) found no correlation between the degree of maturity and the blackening properties of potatoes. Deficiency of potassium (less than 200 lbs. K_20 per acre) produced considerable blackening, while 400 pounds K_20 per acre produced mostly normal tubers.

Tottingham, Ross. and Nagy (45) in similar field experiments using abundant nitrogen and phosphorus and variable amounts of potash found that the potatoes discolored on cocking if less than 300 pounds of potash per acre were used. On the other hand, in a greenhouse trial in which the soil was supplied with abundant nitrogen and phosphorus, low potash (100 lbs. per acre), and some of the less common elements a good crop of potatoes which did not blacken on cooking was produced. The authors believe that perhaps some of the rarer elements help to prevent the discoloration of potatoes.

Following up this lead. Tottingham and Ross (46) grew potatoes in sterile sand to which nutrient salt solutions were added. They found that lack of copper or manganese did not affect the proper development of potatoes. Lack of boron, however, not only reduced the yield 50 percent, but also produced more blackening in boiled potatoes. Beneficial results obtained on addition of potash might be due to the fact that boron is an impurity in potash.

Smith and Nash (36, 37), using Smooth Rural variety tubers as seed, grew potatoes in washed sand supplied with mineral nutrients. The complete mineral nutrient solution contained: KH₂PO₄, Ca(NO₃)₂, MgSO₄, CaCl₂, MnSO₄, Na₂B₄O₇, FeSO₄, and ZnSO₄. Quantities of various nutrient elements were varied. While lack of some elements (Ca, B, Mg, Cu, K) either retarded the growth or showed other symptoms of nutritional deficiency, only the tubers grown in a low potash culture exhibited blackening on cooking.

In the field experiments by the same authors, potatoes were grown in different soils; also, N-P-K ratio of the fertilizer and the amount per acre applied varied (37). In general, no serious discoloration occurred in these experiments. There was, however, some relation between specific gravity, mealiness, and blackening. Higher specific gravity corresponded to mealier potatoes and less blackening. There was also a distinct relation between soil reaction and blackening of potatoes. In the case of the Smooth Rural variety grown in silty clay loam, higher alkalinity of the soil produced better tubers, as shown in Table I.

Table I. Effect of Soil pH on Blackening of Potato Tubers

Soil pH	Extent of Blackening	
4.9	Half surface	
6.4	One-third surface	
7.9	Very little	

Tottingham (47) found that liming of the soil with either CaCl₂ or Ca(OH)₂ had no influence on the color of boiled potatoes.

Cowie (9, 11) claims that insufficiency of potash in the soil will produce discoloration of potato tubers only if high nitrogen is supplied at the same time.

In 1941, Nash (26) tested the cooking quality of ten varieties of New York State potatoes. There was practically no blackening in the tubers from Wayne and Suffolk Counties (early maturing potatoes) but almost all varieties from Steuben and Tompkins Counties (late maturing potatoes) showed some blackening. There

was also a difference in the behavior of different varieties. Green Mountain, Pioneer Rural, and Sebago tubers blackened most seriously, while Houma, Pontiac, and Chippewa blackened the least. In these experiments mealier tubers showed a greater amount of discoloration.

While the time of planting had no consistent effect on the occurrence of blackening, the time of harvesting had a marked effect on the color of boiled tubers (40). Smith and Nash (1942) confirmed the data of Nash (26) that later-harvested tubers darkened to a greater extent than those harvested earlier. Also, mealier potatoes discolored more readily, as shown in Table II.

Table II. Effect of Harvesting Time on Color and Texture of Potatoes

Smooth Rural variety - Planted May 15-June 15

Harvested	8/16	9/7	10/5
Color	9.6*	8, 2	7.0
Texture	4.0**	7.5	8, 5

^{*}Scale of color: 10 - white; 1 - very black

On the basis of 600 samples grown under different environmental conditions Smith, Nash and Dittman (1942) came to the following conclusions (41):

"Various levels or combination of various levels of nitrogen, phosphorus, potassium, lime and manure had no consistent or predictable effect upon the occurrence of blackening...Likewise, soil reaction, soil moisture, soil type, and deficiencies of boron, copper, zinc, manganese and magnesium had no noticeable consistent effect."

Tottingham, Nagy, Ross, Marek and Clagett (1943) after six years growing of potatoes in a greenhouse under controlled conditions concluded (49):

- 1. Differences in rates of supply of the major nutrient elements and of iron and boron did not affect the incidence of darkening of boiled potatoes; neither did the omission of manganese, copper, and zinc.
- 2. The blackening depends primarily on the record of the tubers planted. Discoloration was common in Rural New Yorker and Irish Cobbler varieties but rare in Chippewa and Triumph varieties.
- 3. Stocks producing discoloration were free from common diseases; but since the discoloration is apparently inherited, the presence of a virus or of some unrecognized disease is a possibility.

Wallace and Wain (Great Britain, 1943) obtained the following results (56) on field samples of potatoes:

^{**}Scale of texture: 10 - very mealy; 1 - very soggy.

Table III. Effect of Fertilizers on Color of Cooked Potatoes

Soil Treatment	Color of Cooked potatoes (Color scale: 15 - good: 0 - very poor)		
	<u> </u>	<u>11</u>	
None	4	8	
Stable manure	13	13	
N - P - K	12	12	
P - K	10	12	
N - K	8	7	
N - P	1	5	

These data confirm the association of blackening with potash deficiency, which the authors found to hold especially with high N/K ratio. The figures reveal that blackening can be caused also by phosphorus deficiency.

In the experiments with sand culture and nutrient solutions the results were somewhat different, as shown in Table IV.

Table IV. Effect of Fertilizers on Color of Cooked Potatoes

Treatment	Color
Complete nutrient	9
N omitted	15
K omitted	10
P omitted	0
Ca omitted	5
Mg omitted	10

The results show that most discoloration took place when phosphorus was omitted from the nutrient composition. Purplish and brown discoloration was observed when calcium was omitted. There was practically no blackening in the absence of potash, which emphasizes the difference between field and sand culture.

Rieman, Tottingham, and McFarlane (1944) grew 23 varieties of potatoes in nine widely separated locations in Wisconsin during a five-year period (31). The least blackening after boiling was noted at harvest time, the most blackening occurred after five months storage when the tubers were soft and heavily

sprouted. Most of the boiling tests, however, were made (968 tests altogether) two months after harvest on potatoes kept in storage at 42° F. The authors' conclusion was that the dark cooking tendency of potatoes is inherited. Some varieties (Triumph, Chippewa, Sebago) have the tendency to cook white; the majority (Irish Cobbler, Green Mountain, Russet Rural, and others) turn gray on cooking; Katahdin, Houma and a few others are intermediate between the two.

Pollard, Kieser, Crang, and Wallace (1944) grew potatoes in eight different localities in Great Britain (30). Their results led them to believe that variety controls the blackening phenomenon. Some varieties are resistant to discoloration while others are more susceptible to it. In agreement with several other investigators, they found deficiency of potash in the soil somehow associated with the blackening of boiled potatoes. Pollard, et al., conclude that the choice of suitable varieties would go far toward alleviating the blackening problem.

Wager (1946) determined the average grayness of potatoes of different varieties grown for three successive seasons in various parts of England, Scotland, and Ireland (53). His observations resulted in the conclusion that variety controls the behavior of potatoes toward blackening although some varieties behave differently in different seasons. Wager believes that the soil somehow affects the susceptibility of potatoes to stem-end blackening, but there is no clue as to the soil factors which are responsible.

Bandemer, Schaible, and Wheeler (1947) working with Michigan potatoes found (2) that Green Mountain and Russet Rural varieties exhibited greater discoloration than the Sebago or Chippewa varieties.

Tottingham, Nagy. Ross, Marek. and Clagett (1947) described 9 years' field experiments in growing potatoes under different soil and climatic conditions, and with different fertilizer applications. While cultivation was conducted in six different localities in Wisconsin, the seed potatoes were not only from local stock, but also from other states (Maine, New York, Idaho, Colorado, Minnesota, and Nebraska). On the basis of this extensive study they drew the following conclusions (50), which may well serve as a summary for this section of the review.

- 1. No single factor or combination of factors are uniformly responsible for blackening of potatoes on boiling; rather the experiments emphasize the complexity of the factors governing the phenomenon of blackening.
- 2. Variety more than any other factor governs the blackening of potatoes. Chippewa, Triumph, and Sebago rarely turn black on cooking regardless of the conditions under which they are produced. Rural New Yorker, Irish Cobbler, and some other varieties often cook black.
- 3. Fertilization with macro- and micro-nutrient elements does not insure the production of potatoes that will remain white on boiling. Potassium is the only element which--at high level of application--decreases the blackening of potatoes, but this response is not uniform and any generalization on the subject is unjustified by data thus far accumulated.

RELATION OF CLIMATE AND IRRIGATION TO BLACKENING OF POTATOES

Nash and Smith (27) noted that potatoes grown around Ithaca, New York, had a greater tendency to blacken on cooking than those from certain other sections of the country. It was also noted that the number of cloudy days during the season of tuber formation was much higher in Ithaca than in these other sections. To determine the effect of sunshine on changes in potatoes, Smooth Rural tubers were planted on May 25. From August 17 to September 13, part of each plot was shaded with black percale cloth. The tubers were harvested September 28. While there was some difference in the physical and chemical properties of potatoes grown on shaded as centrasted with those grown on unshaded plots, there was very little blackening in either case, except for the plots which received additional nitrogen fertilizer; tubers from shaded parts of these latter plots showed marked blackening on boiling.

Gardner (15) recommended earlier planting to improve the culinary quality of potatoes. But Nash (26) and Smith and Nash (40) found that the time of planting had no consistent effect on blackening. On the other hand, the time of harvest had a marked effect on the color of boiled potatoes. The authors believe that the temperature and sunshine for 2-3 weeks previous to harvest affect the quality of the tuber. Higher temperature and more sunshine produce better tubers, as shown in Table V. Smooth Rural potatoes were planted May 15-June 16.

Table V. Climatic Condition	ons and	Color of Boiled	Potatoes
Harvested	8/16	9/7	10/5
Color*	9.6	8.2	6.7
Average** max. temp., OF.	74	64	60
Average** min. temp., oF.	52	46	39
% Sunshine**	70	55	49

^{*}Scale: 10 - white; 1 - black

The above results were confirmed by Smith. Nash and Dittman (41), who grew potatoes of different varieties in various parts of New York State and some Katahdins at Gainesville, Florida. Their results are summarized in Table VI.

Table VI. Harvesting Temperature and Color of Cooked Potatoes

Temp. range 3-4 weeks before harvest	No. of Av	Average color rating*	
50-60° F.	113	6.6	
60-70° F.	60	8.6	
70-80° F.	59	9.9	

*Scale: 10 - white; 1 - black

^{**}For two to three weeks before harvest.

Tottingham, Nagy, and Ross (44) in 1936 and Tottingham and Ross (46) in 1938 ascribed the unusually frequent occurrence of blackening in Wisconsin during several preceding years as, at least partly, due to excessive heat and drought during that period. In their later (1943) study of the subject, Tottingham. Nagy, Ross, Marek, and Clagett came to the conclusion that heat, drought, or a combination of these factors did not cause a consistent discoloration of cooked tubers. In 1944 Rieman, Tottingham, and McFarlane (31) admitted that some climatic factors, such as high or low temperature at harvesting time had a great deal of influence on the incidence of blackening. In 1947 Tottingham, Nagy, Ross, Marek, and Clagett (50) on the basis of data collected in various localities of Wisconsin concluded that, in general, a hot and dry season increases the blackening incidence. The hottest station in the State, however, reported least blackening.

Wager (Great Britain 1947). commenting on the results of certain American investigators showing that potatoes dug at higher temperatures produced a lower incidence of blackening, stated (54) that if this were true, most of the British late potatoes dug in October should blacken to a greater extent than the early potatoes dug in July. As a matter of fact, however, the early potatoes grown in sandy soil give rise to a higher average incidence of blackening than the late potatoes grown in silt and clay soils. Actual experiments in 1943 and 1944, while partially confirming the results of Smith et al., indicated that some other factors were present which were responsible for blackening of late potatoes. With regard to the effect of low temperatures, Wager believes that there is a critical temperature perhaps near the freezing point which causes injury to the tubers. These short periods of low temperature rather than a general reduction of the average temperature are responsible for the production of tubers liable to discolor on boiling.

Smith and Nash (39) grew potato tubers on a silt loam soil in plots fertilized with 1000-3000 pounds per acre of 4-8-8 fertilizer. One plot received water only in the form of rain; a similar plot received additional overhead irrigation of 4.5 inches during July, August, and September. There was very little difference in the color of boiled potatoes from either plot.

Ashby (1) claims that a light soil of good physical composition produces the best quality tubers in a moist climate, but a heavy soil may do better in a warm dry climate.

Findlay (14) found no difference between sulfate and muriate of potash as fertilizers in dry seasons; in a rainy season, however, sulfate produced potatoes with better color on cooking.

POTATO STORAGE AND BLACKENING

Gardner expressed the opinion that poor aeration in storage may be one of the factors causing blackening of cooked potatoes. Tottingham et al., (44, 45), however, state that neither the storage temperature (39-70° F.) nor the ventilation affect the blackening of potatoes after cooking. Stored potatoes in an advanced stage of sprouting almost always blacken on cooking. Rieman, Tottingham, and McFarlane (31) found that freshly-harvested tubers kept for a few weeks at room temperature exhibited less blackening than similar samples held at 42° F.

for about two months. Tottingham et al. (50) noticed that the tendency to discolor on boiling appears after about 2 months storage at 40° F. and after about 1 month at 60° F. Felton (13), using potatoes from dry land in Nebraska, kept them in cold storage until March. He then put them in storage at 40, 50, 60, and 70° F. for 7 weeks. Stem-end discoloration was greater in potatoes kept at higher temperature. Smith, Nash, and Dittman (41) studied storage at higher temperatures. Tubers known to blacken on boiling were withdrawn from cold storage (40-50° F.) and placed in storage at 68, 86, and 104° F. Boiling tests gave the following results:

Table VII. Effect of Storage at Higher Temperature on the Color of Cooked Potatoes

Duration Storage,		Color Ra	ating* Aft <u>86⁰</u>	er Stora	age at:
12		5	5.5		6.5
36		5	6		7.5
60		4.5	6		8
84		5	6.5	L.	8
108		5	6.5		9

^{*}Color scale 10 - white; 1 - very black

It is obvious that while no improvement was achieved by storing the tubers at 68 and 86° F., considerable improvement took place after 4.5 days' storage at 104° F.

Wager (54) while admitting that cold storage increases the incidence of blackening, claims that cold storage does not make all lots of potatoes blacken to comparable extent. Better potatoes remain better under different conditions of storage.

POTATO COMPOSITION AND BLACKENING

According to Ashby (1) the percentage of dry matter does not show much relation to quality of potatoes. Bewell, (3) on the contrary, believes that the solids contents of the potatoes determine their cooking quality. He claims that discoloration after boiling occurs mostly in low solids potatoes; the color improves with the increase of total solids of the tubers. Various authors have recommended the use of early potatoes as less subject to blackening; these are usually low in solids content (35). Bandemer, Schaible, and Wheeler (2) determined moisture, ash, manganese, iron, and pH of Sebago, Chippewa, Green Mountain, and Russet Rural varieties of Michigan potatoes. Their results indicate some correlation of moisture and pH with darkening of boiled potatoes. The discoloration increased with increased moisture and decreased pH, perhaps due to hydrolysis of some carbohydrate constituents and their combination with amino acids (nonenzymatic browning reaction). Wager (53) found no relationship between soil pH and tuber pH, and no evidence that pH of the tubers influences stem-end blackening of potatoes.

Ashby (1) analyzed potatoes for total ash, potash, phosphoric acid, lime, magnesia, chlorine, and ferric oxide. Low potash corresponded with potash deficiency in the soil; high chlorine was usually associated with potatoes of poor quality.

Nagy (24) and Tottingham, Ross and Nagy (45) found average K₂O values up to 1.8 percent of the dry matter for blackening potatoes, and a higher figure for normal tubers. Tottingham (47) determined mineral constituents (with parallel cooking tests) on a number of potato tubers grown in different localities of Wisconsin. He concluded that there was no relation between blackening of the tubers and their calcium, iron, boron, copper, and phosphorus contents. Miss Robison (32) found a marked correlation between iron content (as extracted with 20% sulfuric acid) and the incidence of blackening in tubers drawn from the same sample; blackening tubers contained, in every case, more iron than the normal ones. Wallace and Wain (56), as previously stated, found most discoloration when phosphorus or calcium was omitted from the fertilizer. They found in the ash of the same potatoes more iron than in other samples, thus indirectly corroborating Robison's data.

Ashby (1) combined six samples of good quality potatoes from different locations and compared them with six mixed samples of poor quality tubers. In defining "good quality" potatoes, Ashby placed some weight on absence of discoloration after cooking. His figures are in the following Table VIII:

Table VIII. Nitrogenous Matter and Quality of Potato Tubers

Composition	Six good samples	Six bad samples
Dry matter	22,5%	21.2%
Total N	1.29% on dry basis	1.35% on dry basis
Protein N	.53% " " "	.69% " " "
Non-protein N	.76% " " "	.69% " " "
% N in protein form	41.4	50. 9
% N in non-protein form	58.6	49.1

Ashby concluded that a high ratio of non-protein nitrogen to protein nitrogen was characteristic of good quality potatoes.

Merkenschlager (22) suggested that in some years (with high incidence of blackening) more tyrosine is developed in potatoes than in normal years.

Gardner (15) found no relation between nitrogen content of potatoes and the color of boiled tubers. Nagy (24) and Tottingham, Nagy, and Ross (44) explain blackening as due to higher tyrosine and tryptophane contents in abnormal potatoes. They found total nitrogen in tubers that cooked white averaging 1.69 percent (1.08 - 2.94 range); in blackening tubers the average was 1.87 percent (1.48 - 2.22 range). On the assumption that condensation products of sugars and amino acids (tyrosine and tryptophane) might be responsible for the pigmentation of cooked potatoes, the contents of amino acids were determined; it was found that α -amino nitrogen, tyrosine, and tryptophane contents were 10, 25, and 20 percent higher, respectively.

in the blackening than in normal potatoes. The contents of sugars and soluble amino acids remained essentially constant during boiling of non-blackening potatoes, while abnormal potatoes lost some of these constituents. Tyrosine and tryptophane increased appreciably on boiling normal potatoes but remained constant in abnormal tubers. The authors also found that the sap of blackening potatoes is considerably richer in tyrosinase (as measured by tyrosine destroyed) than that of normal potatoes, which might indicate also an enzymatic process as a cause of blackening of potatoes

Smith and Nash (36), growing Smooth Rural potatoes in quartz sand with various nutrients added, found no correlation between a-amino acids, tyrosine and tryptophane content of potatoes, and their discoloration on cooking. On repeating the experiments, however, under more favorable conditions, they observed (37) blackening in samples grown in a low potassium culture accompanied with higher trosine and tryptophane content of potatoes.

Robison (32) found no correlation between the discoloration of potatoes and their tyrosine content, or the activity of tyrosinase.

Nash (26) found no connection between blackening of potatoes and chemical composition represented by the following data: Total solids, starch, starch, protein ratio, total nitrogen, protein nitrogen, tyrosine.

Clagett and Tottingham (8) found no relation between total reducing substances content or ascorbic acid content and the discoloration of potatoes on cooking. There was a proportionality between catechol (or catechol-like substances) content and the darkening of stored cooked potatoes.

MEASUREMENT OF DISCOLORATION

In describing or characterizing the color of cooked potatoes, most of the investigators have visually estimated the degree or extent of blackening or graying and referred to a number or symbol on some arbitrary scale. To make matters more complicated the numbers or symbols indicated in some cases the intensity of the color developed, while in other cases they referred to the fraction of the surface discolored. And sometimes it is hard to tell which of the two definitions the author had in view. To give an idea of the complexity and confusion in this field, various color scales are described below.

Tottingham et al. (44) rated cooked potatoes: o - white, x - gray to black. Clagett and Tottingham (3) used the symbols: o = white, ? = light gray, + = medium gray, ++ = dark gray; also, o = white, ++ = medium gray, +++ = dark gray. Tottingham, et al. (49): W = white, LG = light gray, MG = medium gray. Rieman, Tottingham, and McFarlane (31) used the scale: l = white, 2 = light gray, 3 = medium gray, 4 = dark gray. For a group of tubers "blackening inder" can be figured out with 0 = all white, and 100 = all dark tubers. Tottingham et al. (50): 0 = white, l = light gray, 2 = medium gray, 3 = dark gray; "blackening inder" (for 10 tubers) = sum of scores divided by 0.3. Smith and Nash (38): l = very little darkening to 6 = very dark; the same authors (39): 10 = white to 0 = very black; this scoring was also used by Bownin and Manhing (5). Nash (26): 10 = white to 1 = very black; this was used by Smith and Mash also (40). Wellace and Wain (56): 0 = poor color to 15 = good color. Follard et al. (30): 5 = white to 1 = very black. Wager (51): 0 = white to 4 = dark. Wager (53, 54): 0 = white to 3 = black. Bandemer et al. (2): 6 = white to 3 = very black.

The only objective method of measuring the discoloration of potatoes was made by Bilham, Maunsell. and Lampitt (4). They used a photometer to measure the percentage of light reflected by the cooked potatoes (mashed and packed in a Petri dish). The potatoes were graded as shown in Table IX.

Table IX. Grading of Color of Cooked Potatoes

% Reflection	Grade #
100	0
96-99	0.5
91-95	1.0
86-90	1.5
41-45	6.0

The accuracy of this method is not very high but much higher than could be obtained with the unaided eye.

PREDETERMINATION OF BLACKENING OF POTATOES ON BOILING

It would be of practical value to potato distributors and big consumers of potatoes if tests were available to predict in advance whether blackening will take place during or after processing. Two such tests have been suggested.

Tinkler (43) found that all potatoes examined contained a substance (or substances) which on treatment with nitrous acid followed by an alkali gives a fine red color. The test is carried out as follows. A transverse section of a potato about 5 mm. thick is peeled thinly and covered with about 25 cc. of 7 percent sodium nitrite solution in a small porcelain dish. About 2 cc. of hydrochloric acid (one volume concentrated hydrochloric acid to 2 volumes water) are added and left for five minutes. The liquid is then poured off and the section of potato covered with about 25 cc. of 16 percent sodium hydroxide solution. The red color develops in about five minutes. After some time the red color is extracted by the sodium hydroxide solution. The intensity of color is proportional to the amount of blackening developed after cooking.

The red color disappears on addition of dilute hydrochloric acid and reappears on making the solution alkaline. The red substance is changed or decomposed on heating with hydrochloric acid and the color cannot be restored on addition of alkali. A section of potato soaked in water before the test will develop less color with nitrous acid and will yield still less color if soaked in dilute acid. The author does not give any numerical data on application of this test.

Another test was suggested by Wheeler (57). By means of 3/8" x 6" brass cylinder, three plugs are cut out from the potato tuber through the stem end, the seed end, and the middle portion. One-half inch pieces were cut from the ends of each of the three plugs and placed in a glass tube containing 95 percent alcohol. The middle portions of the plugs were discarded. After an hour in alcohol the plugs were examined. If they remained white and firm the potatoes cooked white. Shrunken and discolored plugs indicated discoloration on cooking.

Several hundred tubers tested in this manner showed a good agreement between the preliminary tests and actual cooking tests.

Ninety samples of table stock potatoes tested in the Michigan Upper Peninsula by both methods gave the following results: In the alcohol test 17 samples were white, 60 slightly discolored, and 13 dark. In the cooking test 17 were white. 64 slightly gray, and 9 dark. It took three hours to complete the alcohol tests and two days for the boiling tests.

Bandemer et al. (2) used Wheeler's test and obtained very good agreement with actual cooking tests.

SUGGESTIONS FOR PREVENTING DISCOLORATION IN COOKED OR PROCESSED POTATOES

Some measures for improving the color of boiled potatoes obviously suggest themselves by the material discussed in previous sections of this review. Most investigators agree that selection of the right varieties will be very helpful in eliminating the discoloration. The right varieties will be different in different localities, but they are known to potato growers to whom, however, the matter of color is merely one of many factors to be considered. Thus in Wisconsin, Tottingham et al. (50) recommended Chippewa, Triumph, and Sebago varieties which rarely cook black. On the other hand, Nash (26) in New York State lists Sebago variety as one that blackens very readily. As least blackening tubers Nash names: Houma, Pontiac, and Chippewa varieties. Earlier planting of earlier maturing varieties will produce mostly nonblackening tubers (40). The early potatoes, however, are usually low in total solids, thus producing a loss for the processor. Exposure of susceptible tubers to 100° F. for 3-4 days will prevent blackening after boiling (40).

Gleason and Marlatt (16) and Nagy and Tottingham (25) recommend soaking of tubers in water preliminary to boiling.

Tinkler (43) noted that while ammonia in cooking water induces more darkening of the potatoes, water acidified with acetic acid produces tubers of better color. The Bureau of Home Economics (7) in its Annual Report for 1933 recommended cooking potatoes in slightly acidified water as a practical method for preventing the discoloration of potatoes. Gleason and Marlatt (16), Hansen (17), Smith, Nash and Dittman (41), and Crang, et al. (12) used various acidic liquids to improve the color of cooked potatoes. Nutting and Pfund (28) found that the discoloration was decreased or prevented by boiling potatoes in water acidified withcutric acid, lemon juice or vinegar to pH 4.1-4.9. They confirmed the observation of some earlier investigators that boiling in acid solutions produces a tough layer on the outside of the tuber.

Smith and Kelly (35) suggested the following procedure for obtaining a light-colored product in dehydration of potatoes: (1) tubers are preheated in water at 165-212° F., (2) peeled, (3) diced, sliced, etc., (4) blanched in water maintained at pH 4 with phosphoric acid for five minutes, (5) rinsed-ready for dehydration. Wager et al. (52) also recommend the use of slightly acidified water for scalding potato strips before lehydration.

In their study of influence of acids on the discoloration of potatoes Bowman and Hanning (5) used ten varieties of potatoes which were classified good, fair,

and poor from the point of view of darkening incidence. All potatoes were carefully graded and stored at 38-42° F. but kept for 10-14 days at room temperature before cooking tests.

The effect of acids and acidic substances (acetic, ascorbic, citric, hydrochloric, tartaric, lemon juice, calcium diphosphate) on reducing the discoloration of potatoes is reversible. Darkening reappears on increase of pH. Boric and benzoic acids inhibit the color development, but their effect is not reversible, perhaps, due to combination of these acids with catechol or other phenolic compounds (?), thus inhibiting the action of tyrosinase. Cream of tartar, in common with other acidic substances, reduces the discoloration but has no detrimental effect on the texture or flavor of potatoes or on the ease of mashing.

After this paper had been prepared for publication, two articles [Ora Smith and Paul Muneta. Amer. Pot. Journ. 31, 404 (1954) and W. Smith Greig and Ora Smith, ibid. 32, 1 (1955)] were published suggesting the use of sequestering and chelating agents in preventing the after-cooking discoloration of potatoes. The above agents were applied either by spraying the foliage of the growing potatoes about six weeks before harvesting or by dipping pre-peeled potatoes in a solution of a sequestering agent 24 hours before boiling. These suggestions are based on the assumption that the discoloration of potatoes is due to the interaction of iron and catechol-like substances of the potato (see Section D of the chapter on Mechanism of Discoloration).

There is unanimous agreement that after-cooking discoloration can be prevented or materially resuced by acidification of the aqueous medium in which the potatoes are boiled. Therefore, the bleaching of the discolored potatoes with acid or the reversibility of the discoloration with pH change can be included in the definition of this phenomenon.

MECHANISM OF DISCOLORATION AND THE NATURE OF COLORING MATTER

- A. The idea that the discoloration of potatoes on cooking might be due to the reaction between amino acids and reducing sugars was casually advanced by Tottingham et al. (44) and Bandemer et al. (2). The nonenzymatic browning, however, is catalyzed by acids, while potato blackening as has been shown is inhibited by the presence of acid.
- B. More has been written on enzymatic browning as the cause of the discoloration of potatoes on cooking. Ashby (1) noticed that freshly rasped material of both the normal and the blackening potatoes changed its color rapidly to red, brown, and finally black. This, according to Ashby, excludes (?) any connection between blackening and the action of tyrosine-splitting exidase which causes the discoloration of raw potato juice.

In 1928 a considerable part of the potato crop in Germany showed a tendency to blacken on cooking. Merkenschlager (22) explained this phenomenon as due to the oxidation of tyrosine by the enzyme tyrosinase and subsequent condensation to melanin. While it is true that the enzyme is destroyed on boiling the potatoes, it is stable up to 75-90°C. Thus a slice of blackening potato thrown in boiling water did not discolor on cooling, but a slice from the same potato put into cold water which was then gradually brought to a boil discolored rapidly on cooling. The warming process expedited the enzyme action. Later, oxygen further oxidized the product of enzyme action to melanin.

Under normal conditions the enzyme is bound in the cell. On injury to the cell due to heat, cold, infection, or mechanical injury, the tyrosinase could be freed for action

Excess of tyrosine in potatoes appears in some years. Deficiency of potash might be one of the causes. It had been shown previously that lack or deficiency of potassium in soil or tubers produces blackening potatoes. Potassium has an important role in the protein synthesis of plants. Perhaps in the absence of potassium an abnormal accumulation of tyrosine takes place.

Tottingham and his collaborators (24, 25, 35, 34, 44) believe that blackening of potatoes is due to weakening in the structure of protein in the tubers. Protein of abnormal potatoes hydrolyzes or autolyzes more readily than that of normal tubers. There is more tyrosine and tyrosinase in blackening tuters. Extracted and purified pigment from blackened potatoes had nitrogen contents close to that of artificially prepared malanin (24). The proportion of amino acids, especially tyrosine and tryptophane, to protein is much higher in abnormal than in normal tubers. Tyrosinase in the presence of air transforms tyrosine into a black pigment—melanin (45). Ross. Tottingham, and Nagy (34) chowed that tyrosinase activity in blackening tubers is higher than that in normal tubers. An activator of tyrosinase was found in the boiled sap of abnormal potatoes. In 1938, Tottingham and Ross (43) showed the beneficial effect of boron in the soil in eliminating the blackening of potatoes. The presence of boron compounds also inhibits the enzymatic oxidation of tyrosine

In 1939 Smith and Nash (37) stated "The blackening of tubers has been fairly definitely associated with the reaction involving the oxidation of tyrosine to melanin"

- C. There are some serious objections to the tyrosine-tyrosinase hypothesis of the discoloration of potatoes on boiling. Miss Robison (52) claims that the black pigment of boiled potatoes is not melanin for the following reasons:
 - 1. The coloration disappears at pH 3 where melanin is stable.
- 2. There was no correlation between pigment development and the activity of tyrosinase (as estimated by the Warburg technique).
- 3. There was no correlation between the intensity of blackening and the tyrosine content of potatoes as determined on a number of varieties.
- 4. The pigmentation develops after heating in alcohol as well as in water, oxygen must be present in either case.

Nutting and Pfund (28) agree that oxidation causes the blackening of potatoes on boiling or baking because potatoes known to blacken will not discolor if cooked in an atmosphere of nitrogen. They believe, however, that the oxidation is not enzymatic because the temperature inside potatoes during cooking was 98°C., and tyrosinase is destroyed by heating at 75°C. for ten minutes. This argument was foreseen and answered by Merkenschlager (22). More valid is their contention that the pigment developed during cooking is not melanin because formation of melanin is retarded at pH 9 and ceases at pH 10 while the discoloration of cooked potatoes is intensified in an alkaline medium. Mrs. Nutting (29) also

compared artificially prepared melanins with the dark pigments of blackened potatoes and found them different both in solubility and in ultra-violet absorption spectra. She also chromatographically separated the extract from the blackening potatoes into two pigments. One was a yellow pigment related to flavones and identical with the pigment obtained from normal potatoes. The other was rather unstable gray pigment related to the yellow flavone pigment. The discoloration is perhaps due to the interaction of flavone pigment with metal giving a flavone-metal complex.

Wager (Gr. Britain, 1945) worked with potato strips which were washed, scalded in boiling water to inactivate the enzymes, and dried at 60° C. These strips still developed color on cooking. The discoloration which he obtained was not bleached by addition of sodium sulfite. Thus, in one experiment he obtained the following results (51):

Table X. Discoloration of Blanched Potato Strips

	Grayness (0 = white, 4	= dark)
pH of	Sample A	Sample B
Cooking	Scalded at	Scalded at
Solution	pH = 7.6	pH = 5.7
4.8	0.0	0.2
5.8	0.2	0.2
6.8	1.7	1.4
7.5	2.2	2. 2

The development of color in this case was obviously not due to tyrosine-tyrosinase reaction. It was due to a pigment whose color was reversibly affected by pH. A water extract from cooked blackening strips was purified by repeated precipitation with alcohol and concentrated in vacuo at 40°C. It was pale brown-yellow when acid, brownish-blue at pH 4-7.5, and bright yellow-brown at pH 11-12. Wager brings out further evidence that this type of blackening was not due to melanin in the following experiment: Part of the potato strips were allowed to discolor by enzymatic oxidation before scalding so that gray colored, dry strips were obtained. A control batch of dried strips was also prepared. Both were cooked in solutions of various degrees of acidity with the following results:

		Grayness	
pH of Cooking Liquid	Melanin Strips	Control	Difference
3.5	2.1	0,1	2.0
5. 2	2.5	0.1	2.4
6.1	2, 8	0,2	2, 6
7.0	2.9	0.7	2.2
7.6	3.2	1.2	2.0

Since the color of melanin does not change within this range of pH, the approximately constant difference between the two ratings is due to melanin, and the stem-end blackening is due to an entirely different pigment.

Also it might be added here that tyrosine-tyrosinase reaction proceeds through red, brown, and black stages of coloration, it never produces an intermediate blue color often observed in blackening potatoes.

D. Another hypothesis advanced by various investigators to explain the discoloration of potatoes is that catechol or catechol-like substances or tannin and tannin-like compounds might be responsible for the stem-end blackening of the potatoes. Ashby (1) suspected it. He analyzed his normal and abnormal potatoes for tannin and tannin-like materials, found no difference in their content, and concluded that blackening was not due to tannins. None of his potatoes, however, exhibited very distinct blackening.

Tinkler (1931) believes that blackening of potatoes is due to oxidation. If cooked potatoes known to blacken are placed, immediately after boiling, in an atmosphere free of exygen, no blackening will take place (45). Normal potatoes cooked in the presence of rusting iron blacken after cooking. The action is due either to catalytic premetion of exidation, or to the combination of iron with phenolic compounds to produce colored substances. Ammonia in cooking water induces more darkening in the potato perhaps due to promoting atmospheric oxidation of polyhydric phenols.

Bureau of Home Economics (1933) workers came to the conclusion that the potato constituents responsible for blackening belong to the catechol type tannins (7).

As stated above, Ross, Tottingham, and Nagy (34) found a tyrosinase activator in the sap of blackening potatoes. Since it has been known that catechol had an activating effect on a tyrosinase system, and also that lack of darkening in the Sunbeam variety of peaches on exposure of their sliced tissue to the air was due to deficiency of catechol-tannin compounds, Clagett and Tottingham (1941) investigated the influence of phenolic compounds on the discoloration of potatoes (8). Some of their results are given in the following table. The color scale they used was: 0 = white, the medium gray, the dark gray, d = mildly discolored cortex, D = seriously discolored cortex. Catechol compounds seem to be localized in the cortical region.

Rural New Yorker Potatoes: Sample	Catechol, Milligrams per 100 g. Tissue	Discoloration After Cooking
1	4.6	0
2	4.8	++
3	5.4	€. ++
4	6.2	++
5	5.8	++D
6	6.2	++D
7	7.3	+++

Other experiments with different varieties of potatoes confirmed these results. In the same year, Tottingham and Clagett (48) expressed the opinion that oxidation of catechol by polyphenolase is a primary cause in darkening of boiled potatoes. In 1942. Smith, Nash, and Dittman (41) suggested that hydroxybenzene

compounds found in potatoes might be responsible for producing colored compounds.

Thus, the catechol hypothesis can be subdivided into three parts. As an activator for tyrosinase, catechol is a part of the tyrosine-tyrosinase scheme of discoloration of potatoes. Secondly, catechol, in combination with iron or other metals, might produce colored compounds in the potato. And finally, the discoloration might be due either to chemical or enzymatic oxidation of catechol and similar compounds.

E. As described in the section on "Potato Composition and Blackening," Miss Robison (32) found more iron in the blackening than in normal potatoes. Non-blackening tubers can be made to blacken by soaking them for a few days in one percent ferrous sulfate solution, washing off the excess of salt and boiling. The color thus produced is even more intense than that observed in ordinary blackening tubers. It could be bleached at pH 3. The following tentative hypothesis has been advanced.

"In the raw tubers the precursor of the black pigment exists in the form of ferrous iron bound in a loose complex possibly in combination with proteins. This complex is hydrolyzed on boiling and the iron is then precipitated as white ferrous hydroxide and is gradually oxidized passing through green to the magnetic black oxide."

While there is no direct evidence to support this hypothesis, it agrees with the facts and has some support in the work of Tinkler (43) who induced blackening in normal potatoes on boiling them in the presence of rusting iron. It is also supported somewhat by the results of Wallace and Wain (56) who found more iron in the ash of blackening potatoes than in that of normal tubers. Ross and Tottingham's (33) observation that proteins of blackening potatoes are more readily hydrolyzed or autolyzed than those of normal potatoes falls somewhat in line with Robison's idea of a loose iron-protein complex.

Cowie (10), commenting on Miss Robison's hypothesis, connects it with the known fact that potatoes grown on potash-deficient soil in association with rather high nitrogen discolor readily on boiling. Also, in potash-starved plants the amino acids occur in increased amount relative to the protein, probably due to premature breakdown of proteins. This in turn might cause an abnormal distribution of iron in the plant. Thus in corn grown under conditions of potash deficiency, the iron accumulates in the node tissue with resulting dark purplish brown coloration and breakdown of the tissue. Cowie suggests the study of K/Fe ratio in normal and abnormal tubers.

F. In 1947 Lewis and Doty (21) isolated from potatoes by extraction with acidified alcohol a colorless fluorescent substance which, they believe, is the precursor causing blackening in boiled potatoes. The substance which they isolated and purified is an unsaturated compound which readily adds bromine to its molecule. It contains a carbohydrate group (positive Molish test) with a free carbonyl group (reacts with 2,4-dinitrophenylhydrazine); also present is a nitrogenous amino acid or peptide group (positive ninhydrin test after hydrolysis with 20% HCl) but not tyrosine or tryptophane (negative Millon test). On bromination or reaction with 2,4-dinitrophenylhydrazine, nonfluorescent derivatives were obtained. Ultraviolet absorption spectra curves of the fluorescent preparations showed a maximum at 2800 A°.

The fluorescent substance is readily converted into a black pigment at temperatures above 35°C even in acid solutions and in an atmosphere of carbon dioxide. It turned black instantly in alkaline solutions. There is no positive evidence that the substance isolated is the precursor of the black pigment of boiled potatoes. Also, the authors do not state whether the potatoes used in their experiments were of the blackening type. The fact that the fluorescent material blackened even in acid medium and in the absence of oxygen contradicts the only data on which all previous investigators are in agreement. It is possible, in the opinion of this reviewer, that Lewis and Doty's substance is the precursor of humin and the nonenzymatic browning of food products.

Bowman and Hanning (6) repeated Lewis and Doty's work and isolated the same mateial. They also measured the "fluorescence equivalent" (computed as micrograms equivalent of quinine sulfate) for blackening and nonblackening potatoes. Their data showed:

Potato tubers after cooking White Slightly gray Moderately dark Very dark Fluorescence Equivalent 0.4 - 1.7 0.9 - 5.1 0.8 - 5.9 1.1 -10.5

While in a general way the darkening of potatoes after boiling increased with the increase of fluorescence equivalent, the overlapping of the figures is too great to permit prejudgment of the behavior of potatoes on cooking. Thus in one case out of six tubers with fluorescence equivalent of 1.7 one tuber cooked white, one very dark, and four showed moderate darkening. In another case, the fluorescent material from two lots of Russet Burbank potatoes (one from Idaho and the other from Wisconsin) showed identical ultraviolet absorption spectra. Both the alcoholic extracts and the precipitates darkened very readily. On the other hand, the Idaho lot cooked white, while the Wisconsin lot darkened on cooking. The authors concluded that their experiments indicated no clear relationship between the fluorescence and the tendency of certain potatoes to turn dark on cooking.

G. Thus far the various hypotheses described failed to explain one important aspect of the problem, viz., why does the discoloration start usually at the stem-end of the tuber. The only obvious explanation of this phenomenon would be the localization of some chemical or chemicals at this point of the tuber. It is surprising, therefore, that practically no work on comparative analysis of different parts of the potato tuber in connection with the blackening phenomenon is on record. Smith, Nash, and Dittman (41) and Wager (53) determined the acidity of the stem end as compared with other parts of potato. They found the stem end slightly more acid than the rest of the potato but the difference was very small (0.1-0.2 pH).

A purely speculative hypothesis on the subject was advanced by Wager (54). He believes that the potato tops before dying supply (through the stem end) to the tuber the precursor of the pigment responsible for the discoloration of potatoes. This might explain the fact that the tubers harvested early blacken less readily than those dug after the vines are gone.

SUMMARY

Neither the chemical analyses of soil nor those of potatoes have thus far produced any generally acceptable clues to the mystery of the after-cooking discoloration of potatoes. Study of the fertilizers added to the soil resulted in almost general acceptance of the fact that high potash is desirable for improving the cooking quality of potatoes. There seems to be almost a unanimous agreement that certain varieties produce better results than others. These "good" varieties are, however, different for different localities. Lack of uniformity in measuring or estimating the extent of discoloration has been brought out. There is a general agreement that the discoloration is a function of pH. At pH below 5 no after-cooking blackening takes place. Consideration of the experimental data and of the various mechanisms advanced to explain the after-cooking discoloration seems to prove that the stem-end discoloration is a phenomenon distinct from enzymatic and non-enzymatic browning as they are ordinarily understood. On the other hand, there is no reason why one or both of the latter reactions might not take place simultaneously with the stem-end discoloration, which adds to the complexity of the problem.

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